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Developing a highly sensitive electrochemical sensor for malathion detection based on green g-C₃N₄@LiCoO₂ nanocomposites

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Nowadays, developing pesticide-free agriculture is highly demanded by society. The development of electrochemical sensors to monitor and control pesticides is an effective step toward this desired goal. The current research has faced this issue by modifying of glassy carbon electrodes (GCEs) with green g-C₃N₄@LiCoO₂ nanocomposites to probe malathion, an organophosphate pesticide. The g-C₃N₄@LiCoO₂ modified GCE showed higher current than the net GCE, as a result of improved electrocatalytic performance of the modified GCE to oxidize malathion. Increased malathion concentration enhanced the malathion oxidation anodic peak current at +410 mV caused by the g-C₃N₄@LiCoO₂ modified GCE. The developed probe showed an excellent linear response for malathion detection in the 5–120 nM ($R^2 = 0.994$) range and recorded a limit of detection of 4.38 nM. Besides, the modified GCE reveals considerable stability and reproducibility, which offers a cost-effective, sensitive, and selective electrode for malathion probing.

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1. Introduction

Organic pesticides (OPs) such as organophosphorus are commonly used to safeguard crops from pests.^{1,2} These potent molecules pose a significant risk to humans and animals, as they can be absorbed by living organisms through various harmful pathways. Another group of harmful organic compounds is organochlorine insecticides, which can have devastating effects on all life forms, leading to environmental degradation and ecosystem pollution. Malathion, in particular,

when used in large quantities, can be extremely harmful, impacting aquatic organisms, vertebrates, and humans by disrupting neurological functions, causing adverse effects such as headaches and nausea, and significantly compromising immune systems. Not only does it pose a threat to living beings, but it also contaminates agricultural produce and groundwater. Consequently, detecting OPs requires a precise, rapid, sensitive, and dependable analytical approach.^{2–5} Lately, individuals have innovated various detection techniques like GC,⁶ HPLC,⁷ MS,⁸ and ECL.^{9,10} Of these, ECL sensors have garnered significant interest because of their straightforward usability, heightened sensitivity, and cost-effectiveness. This method excels in swift detection processes. A chemical sensor, as per the IUPAC¹¹ definition, is a tool that transforms chemical information, spanning from the levels of an individual substance in a sample to a comprehensive analysis of its composition, into a signal suitable for analysis. Primarily, a chemical sensor comprises two key components: a receptor and a physicochemical transducer. Receptors exhibit variability and can include activated or doped surfaces and intricate (macro) molecules that establish highly precise connections with the substance being analyzed. Catalytic sensors leverage catalytic processes to produce the signal.¹² As the dominant players in the market, electrochemical sensors are widely used primarily because of their benefits, such as their ability to achieve low detection limits, sometimes as minute as picomoles.¹³ The increasing need for trace pesticide detection methods that are quick, precise, sensitive, easy to use, and durable compared to traditional methods is evident.^{14–18}

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This demand has been somewhat met by employing various strategies, including non-enzymatic electrochemical detection, a fairly efficient and promising platform for sensing pesticides.^{19,20} The utilization of new and sophisticated sensor materials in agricultural settings is currently in its initial phases of advancement compared to other fields.^{21–25} Through the progress of sensors and diagnostic tools for on-site monitoring, farmers will be able to observe environmental factors crucial for plant growth and protection closely. By detecting issues early, these monitoring systems can improve productivity while minimizing the need for agricultural chemicals.^{26,27} Recent breakthroughs in innovative functional materials include metal-free substances like RGO and $g\text{-C}_3\text{N}_4$.^{28–31} Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a metal-free semiconductor, is recognized for its composition—a graphitic π -conjugated layered structure substituted with nitrogen. This structure comprises aromatic heptazine units linked by tertiary amines.^{32,33} Due to its unique optical, electronic, and physicochemical properties, $g\text{-C}_3\text{N}_4$ has become a desirable candidate for a variety of applications such as solar water splitting, degradation of pollutants using visible-light photocatalysis, optoelectronics, SERS sensing, and bioimaging.^{33–38} Nevertheless, the constrained conductivity and significant contact resistance of $g\text{-C}_3\text{N}_4$ impede its effectiveness in electrocatalysis, limiting its use in electrochemical fields.

The inherent structure of $g\text{-C}_3\text{N}_4$ includes numerous consistent nitrogen centers that can function as active catalyst sites in electrocatalysis. This implies that modifying $g\text{-C}_3\text{N}_4$ appropriately could significantly enhance its electrocatalytic performance. Structural modification can involve various methods, such as doping, composite formation, and nanostructuring. Among these methods, creating $g\text{-C}_3\text{N}_4$ composites with different materials possessing superior electronic and electrochemical properties, like metal nanoparticles, metal oxides, and semiconductors, is a promising strategy to enhance the electrocatalytic properties of $g\text{-C}_3\text{N}_4$. In sensor exploration, creating an electrochemical sensor that exhibits enhanced selectivity, sensitivity, reproducibility, stability, and detection limit for specific pollutants remains challenging. In this study, we address the critical need for sensitive and reliable malathion detection by developing an electrochemical probe based on green $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposites. Our approach leverages the synergistic properties of $g\text{-C}_3\text{N}_4$ and LiCoO_2 to create a composite material with enhanced electrocatalytic performance. The $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ modified GCE demonstrated significantly improved electrocatalytic performance for malathion oxidation compared to bare GCE. The optimized sensor exhibited a linear response for malathion detection in the range of 5–120 nM with a low detection limit of 4.38 nM. Electrochemical studies revealed that incorporating LiCoO_2 into $g\text{-C}_3\text{N}_4$ enhanced electron transfer kinetics and increased the electroactive surface area, improving sensitivity, selectivity, and stability. This work contributes to the advancement of pesticide-sensing technology and aligns with the growing demand for sustainable agricultural practices. Our innovative sensor design shows great potential for practical applications in environmental monitoring and food safety, representing a significant

step towards developing efficient, cost-effective, and green solutions for pesticide detection. Ultimately, this research supports the transition to pesticide-free agriculture while promoting public health and environmental protection.

2. Experimental

2.1 Green synthesis of LiCoO_2 nanoparticles

LiCoO_2 nanoparticles (NPs) were synthesized through a green process that utilized *Aloe vera* plant extract as a capping agent. 40 g of cleaned *Aloe vera* leaves were finely cut to extract their gel. The obtained gel was diluted with 100 mL of deionized water (DI) *via* sonication for 30 minutes, followed by stirring at 60 °C for two hours. Then, two mmol of each cobalt acetate and lithium acetate were dissolved in 15 mL of DI while stirring for 45 minutes at 60 °C. The obtained solution was mixed with *Aloe vera* extraction solution, followed by refluxing at 70 °C for 24 hours. The refluxed solution was poured into a beaker and heated at 90 °C until a purple paste was obtained. The resultant paste was spread in a ceramic crucible and baked at 750 °C for three hours.

2.2 Synthesis of $g\text{-C}_3\text{N}_4$ nanosheets

15 g melamine (Sigma Aldrich, 99%) was added into 40 mL ethanol (Merck, 99.5%), followed by sonication for 30 minutes at room temperature (RT). Then 500 mg of ammonium sulfate (Merck, 99.5%) was added to the melamine solution and stirred at RT for four hours. After drying the mixed solution in an oven for 12 hours at 50 °C, it was transferred into a ceramic crucible and heated to 500 °C with a 5 °C min^{-1} ramp under an inert ambient, then raising the temperature to 550 °C and keeping for two hours at 550 °C. The cooled product was ground to obtain $g\text{-C}_3\text{N}_4$ nanosheets.

2.3 Preparation $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposite

In four individual vials, 600 mg $g\text{-C}_3\text{N}_4$ material was dispersed into 200 mL DI *via* sonication at RT for two hours. In each vial, different weight ratios of 0.4, 0.8, 1.6, and 3.2% of LiCoO_2 NPs, respectively, were added to them, followed by stirring at RT for two hours. The obtained suspensions were separately poured into a Teflon-lined autoclave and baked at 140 °C for six hours. The $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanostructures were washed with DI and ethanol *via* vacuum filtration. The pre-washed solids were dried in an oven at 80 °C overnight. The prepared $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanostructures based on 0.4, 0.8, 1.2, and 3.2% of LiCoO_2 NPs are labeled with GL1, GL2, GL3, and GL4, respectively.

2.4 Electrode preparation

Polished and washed glassy carbon electrodes (GCEs) with a diameter of 3 mm were coated with prepared materials in this study ($g\text{-C}_3\text{N}_4$, LiCoO_2 , GL1, GL2, GL3, and GL4). For this aim, 5 mg of the synthesized materials were dispersed in 3 mL of ethanol by sonication for 45 min at RT. Next, 6 μL of the above suspensions were dropped cast on net GCEs and dried at RT overnight to form modified GCEs. Then, to conduct the electrochemical tests, including CV, EIS, and DPSV, a three-



electrode cell was employed, in which a platinum electrode, Ag/AgCl electrode, and net GCE or modified GCE were used as a counter, reference, and working electrodes, respectively.

2.5 Materials characterization

Electrochemical investigations were conducted on a CHI760E workstation potentiostat. Philips X'PERT diffractometer recorded X-ray diffraction (XRD) patterns of samples. Solid morphologies and energy-dispersive X-ray spectroscopy (EDS) of samples were investigated using TESCAN MIRA3 FESEM equipment. JEOL JEM-2100 TEM microscope was used to further investigation on morphologies of materials. The SAM 800 X-ray photoelectron spectrometer collected XPS spectra of samples. Gemini 2360, Micromeritics Instruments Corp system conducted nitrogen adsorption-desorption analyses to investigate the specific surface area and pore diameter of samples.

3. Results

Fig. 1 shows a detailed diagram of the synthesis process for $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposites, illustrating various steps, including mixing, heating, refluxing, and baking at different temperatures and durations.

The phase formation of all synthesized specimens was confirmed using X-ray diffraction (XRD) analysis (Fig. 2a). The broad diffraction peaks at 12.74° and 27.32° in Fig. 2a(i) correspond to the (100) and (002) planes of $g\text{-C}_3\text{N}_4$ sheets, respectively.^{39,40} All diffraction peaks in Fig. 2a(ii) are indexed to LiCoO_2 , indicating a typical $\alpha\text{-NaFeO}_2$ structure with space group $R\bar{3}m$.^{41,42} The XRD patterns of the GL1, GL2, GL3, and GL4 composites (Fig. 2a(iii)–(vi)) show diffraction peaks associated with both LiCoO_2 and $g\text{-C}_3\text{N}_4$, confirming the successful synthesis of these composites. The Raman spectra of the synthesized $g\text{-C}_3\text{N}_4$ nanosheets (Fig. 2b) exhibit characteristic peaks that align well with those reported in the literature.⁴³ The distinct E_g and A_{1g} vibrational modes at 488 and 598 cm^{-1} , respectively, in the LiCoO_2 Raman spectrum (Fig. 2b(ii)) are assigned to the asymmetric bending mode of O-Co-O and the

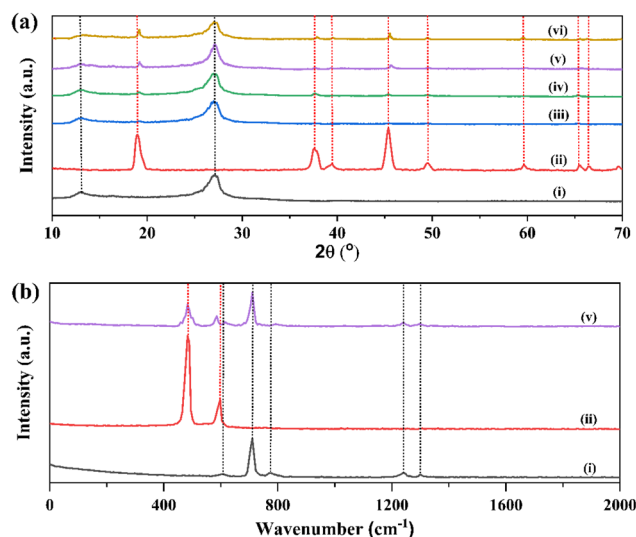


Fig. 2 (a) XRD pattern and (b) Raman spectra of different samples. (i) $g\text{-C}_3\text{N}_4$, (ii) LiCoO_2 , (iii) GL1, (iv) GL2, (v) GL3, and (vi) GL3.

symmetric stretching mode of Co-O .⁴⁴ The Raman spectrum of GL_3 (Fig. 2b(v)) indicates that adding $g\text{-C}_3\text{N}_4$ does not significantly alter the crystalline structure or purity of LiCoO_2 , consistent with the XRD results. The shift of the peak at approximately 598 cm^{-1} in the Raman spectrum indicates a change in the Co-O bond vibration, suggesting due to the interaction with $g\text{-C}_3\text{N}_4$.

The $g\text{-C}_3\text{N}_4$ nanoplates FESEM image reveals a sheet-like morphology, confirming the nanoplate structure of the synthesized $g\text{-C}_3\text{N}_4$ (Fig. 3a). The LiCoO_2 nanoparticles FESEM image shows a collection of spherical particles (Fig. 3b). The $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposites FESEM image demonstrates the successful formation of the hybrid material. The LiCoO_2 nanoparticles are observed to be well-dispersed and intimately anchored on the $g\text{-C}_3\text{N}_4$ nanosheets, suggesting a promising composite structure (Fig. 4c). The EDX pattern of the $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposite is shown in Fig. 3d. The spectrum

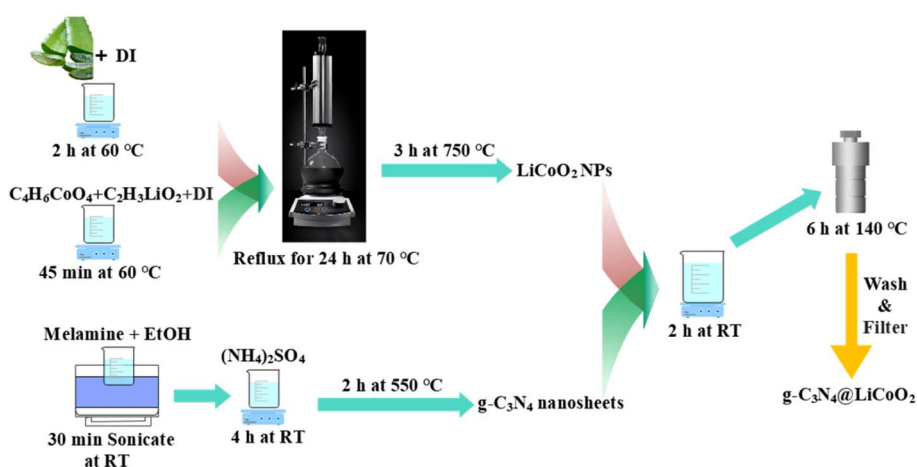


Fig. 1 Schematic view of synthesis process for $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposites.



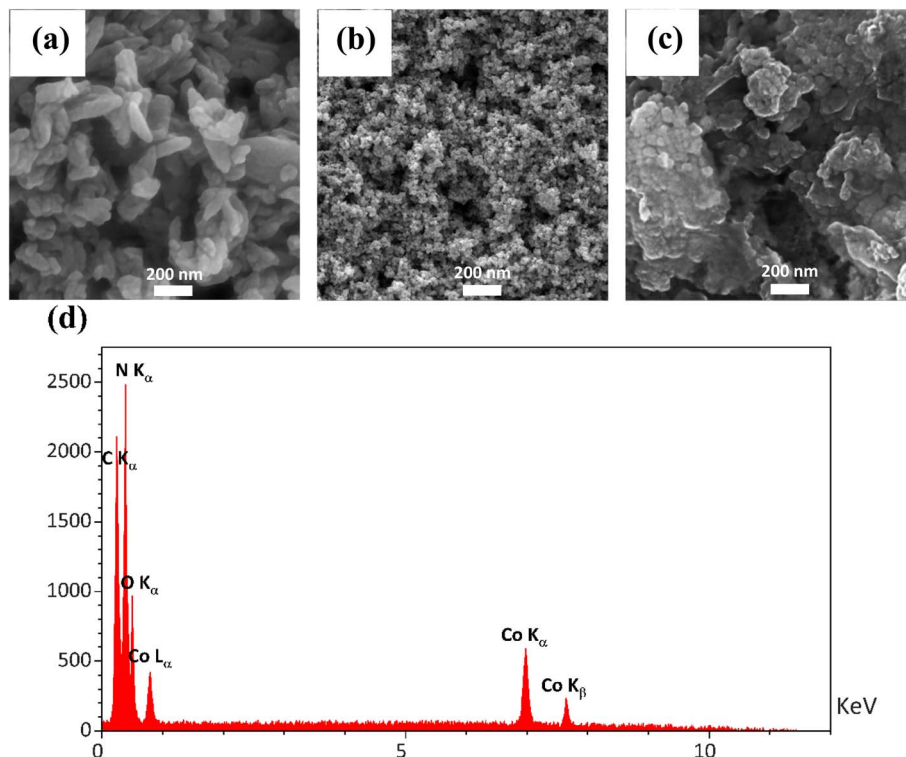


Fig. 3 FESEM image of (a) g-C₃N₄ nanoplates, (b) LiCoO₂ nanoparticles, and (c) GL3 hybrid materials. (d) EDX spectra of GL3 sample.

verifies that the g-C₃N₄@LiCoO₂ nanocomposite contains components like Co, O, C, and N.

The morphology of the as-synthesized g-C₃N₄, LiCoO₂ nanoparticle and g-C₃N₄/LiCoO₂ nanocomposites were characterized by TEM. Fig. 4a clearly illustrated that the as-obtained g-C₃N₄ samples are nanosheets. Fig. 4b clearly illustrates small spherical structure of LiCoO₂ nanoparticles. Fig. 4c show LiCoO₂ nanoparticles with average size of ~25 nm, anchored on the g-C₃N₄ nanosheet are evident.

XPS analysis investigated the elemental composition and valence states in the g-C₃N₄@LiCoO₂ nanocomposites. The XPS spectrum in Fig. 5a confirms the presence of Li, Co, O, N, and C elements in the nanocomposites without any impurities. In Fig. 5b, the Co 2p spectrum displays a Co 2p_{3/2} main peak at 778.1 eV with a satellite peak at 786.5 eV, along with a Co 2p_{1/2}

main peak at 794.6 eV with a satellite peak at 800.1 eV. The ratio of Co 2p_{3/2} to Co 2p_{1/2} is approximately 2/1, indicating the presence of Co³⁺ atoms in the synthesized products.^{45–48} The peak of Li 1s photoelectrons observed at a binding energy of 55.4 eV confirms the presence of Li (Fig. 5c).⁴⁹ Additionally, Fig. 5d illustrates distinct peaks in the GL3 composite at 284.7 eV for C–C bonds and 288.1 eV for N=C–N bonds. The N 1s spectrum in Fig. 5e reveals peak positions for carbon, nitrogen, and hydrogen (C–N–H) bonds at 401.2 eV and C–N=C bonds at 398.9 eV.⁵⁰ The characterization data for the GL₃ electrocatalyst confirm the successful synthesis of the nanocomposite using a straightforward method.

The results obtained from BET measurements are depicted in Fig. 6. The pure g-C₃N₄ and GL3 nanocomposites exhibit significant hysteresis in the relative pressure range of $0 < P/P_0 <$

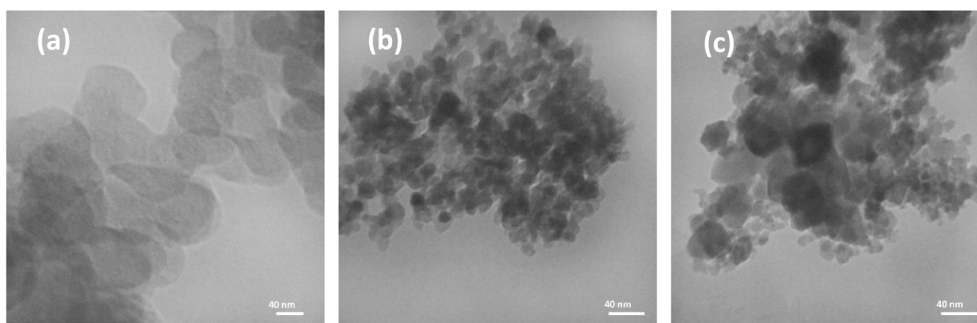


Fig. 4 TEM image of (a) g-C₃N₄ nanoplates, (b) LiCoO₂ nanoparticles, and (c) GL3 hybrid materials.



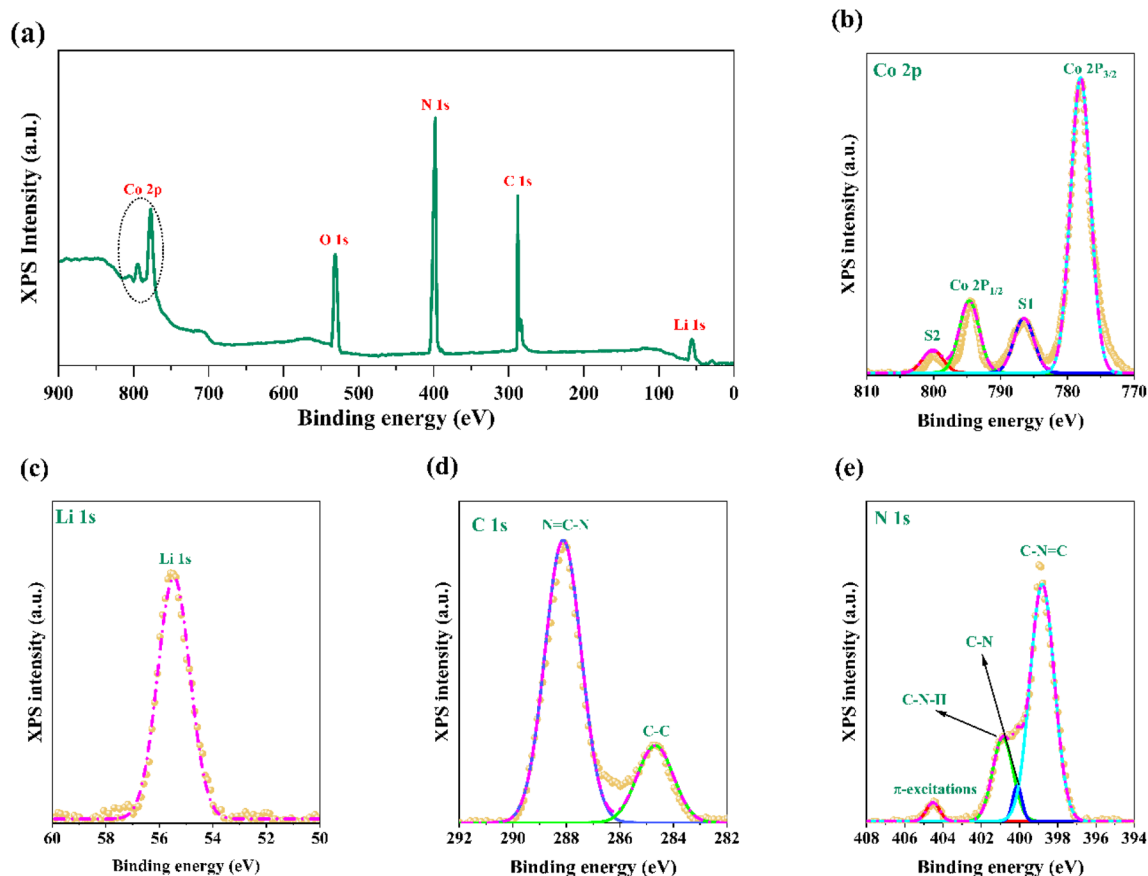


Fig. 5 (a) XPS spectra of GL3 sample. High-resolution XPS for (b) Co 2p, (c) Li 1s, (d) C 1s, and (e) N 1s elements.

1, as shown in Fig. 6a and b. Compared to the pure $g\text{-C}_3\text{N}_4$ with a surface area of $15.81 \text{ m}^2 \text{ g}^{-1}$ and average pore size of 11.649 nm , the GL3 nanocomposites have a higher specific surface area of $23.74 \text{ m}^2 \text{ g}^{-1}$ and average pore size of 8.727 nm . This increase could be advantageous for concentrating target substances in subsequent electrochemical sensing applications.⁵¹

The electrochemical performance of $g\text{-C}_3\text{N}_4@\text{LiCoO}_2$ nanocomposites was evaluated using cyclic voltammetry (CV) and

electrochemical impedance spectroscopy (EIS). Fig. 7a and b depict CV curves obtained at a scan rate of 50 mV s^{-1} . All measurements were performed in a 0.1 M KNO_3 solution containing $2 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$. The CV curve for $g\text{-C}_3\text{N}_4/\text{GCE}$ exhibited small, approximately symmetrical redox peaks at 294 mV and 67 mV , representing the anodic (E_{pa}) and cathodic (E_{pc}) peaks, respectively. The CV curve for GL3/GCE displayed a more prominent pair of redox peaks, with E_{pa} at 366 mV and E_{pc} at 279 mV . This suggests that incorporating LiCoO_2 into the

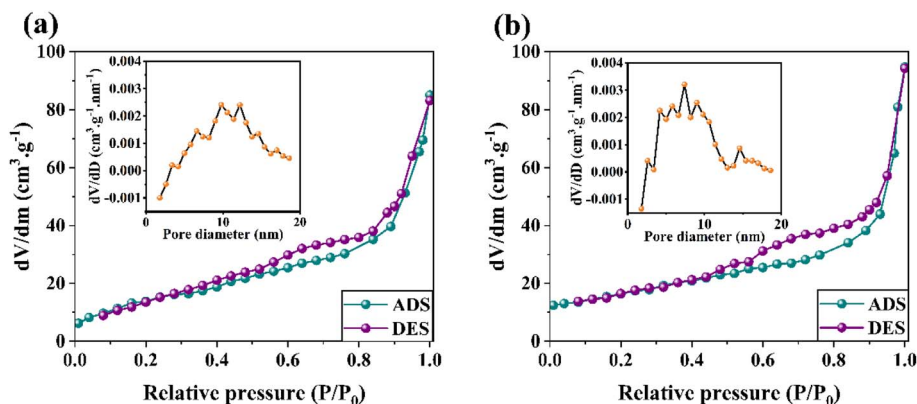


Fig. 6 N_2 adsorption–desorption response and BJH pore size distributions of (a) $g\text{-C}_3\text{N}_4$ and (b) GL3 samples.



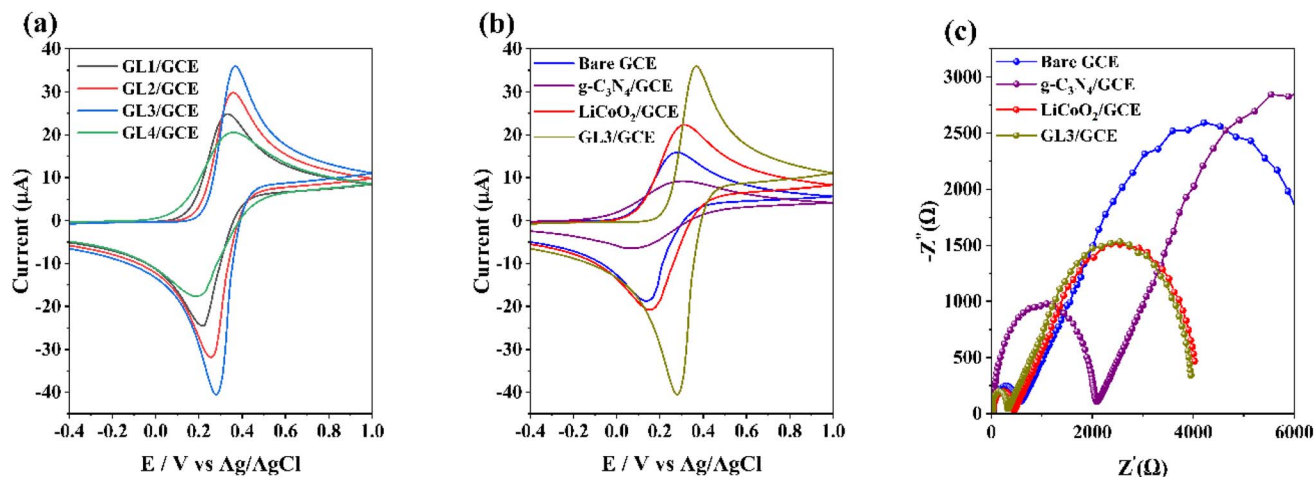


Fig. 7 (a) CV curves of different $g\text{-C}_3\text{N}_4@LiCoO_2/GCEs$ at scan rate 50 mV s^{-1} : GL1, GL2, GL3, and GL4. (b) CV curves of bare GCE, $g\text{-C}_3\text{N}_4/GCE$, $LiCoO_2/GCE$, and $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ (GL3/GCE) at scan rate 50 mV s^{-1} . All tests were conducted for $2\text{ mM K}_3[Fe(CN)_6]$ in 0.1 M KNO_3 solution. (c) Nyquist plot of EIS for bare GCE, $g\text{-C}_3\text{N}_4/GCE$, $LiCoO_2/GCE$, and $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ (GL3/GCE).

$g\text{-C}_3\text{N}_4/GCE$ enhanced the electrochemical activity. Compared to $LiCoO_2/GCE$ and $g\text{-C}_3\text{N}_4/GCE$, the GL3/GCE exhibited a more negative oxidation potential and significantly higher peak currents. This indicates that the $LiCoO_2$ component improved the electron transfer kinetics and increased the electroactive surface area. The peak currents of GL3/GCE gradually increased with increasing amounts of $LiCoO_2$, suggesting that the $LiCoO_2$ component played a crucial role in enhancing the electrochemical activity. However, excessive $LiCoO_2$ doping in GL4/GCE slightly decreased the peak currents, possibly due to the shielding of active sites on the $g\text{-C}_3\text{N}_4$ surface. Overall, GL3/GCE demonstrated the highest charge transfer efficiency and the best electrochemical activity among all the investigated electrodes. This makes it a promising candidate for sensing applications. Incorporating $LiCoO_2$ into the $g\text{-C}_3\text{N}_4/GCE$ composite significantly enhanced its electrochemical properties. The optimized GL3/GCE exhibited superior charge transfer kinetics and electrocatalytic activity, making it a promising material for sensing applications.

The Nyquist plot provides insights into the interfacial charge transfer kinetics and the resistance of the electrode–electrolyte interface. The Nyquist impedance graphs for $LiCoO_2/GCE$, $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ (GL3/GCE), and $g\text{-C}_3\text{N}_4/GCE$ are displayed in Fig. 7c. A reduced arc radius signifies enhanced charge migration efficiency across the electrode–electrolyte interface, with the electron-transfer resistance behavior on the electrode surface being mirrored by the arc radius at elevated frequencies.^{32,52} The Nyquist plot of the GCE revealed a confined

semicircular region, as illustrated in Fig. 7c, indicating minimal electron transfer resistance on its surface. The arc radius grew following $g\text{-C}_3\text{N}_4$ coating, suggesting $g\text{-C}_3\text{N}_4$ inhibited electron transfer. The arc radius of the resulting GL3/GCE demonstrated a noticeable, progressive decrease if the $g\text{-C}_3\text{N}_4/LiCoO_2$ nanocomposites were coated, suggesting that the $LiCoO_2$ can reduce the interfacial resistance. The charge transfer resistances for the bare-GCE, $g\text{-C}_3\text{N}_4/GCE$, $LiCoO_2/GCE$, and $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ are measured at $487.3\ \Omega$, $1984.5\ \Omega$, $398.7\ \Omega$, and $264.6\ \Omega$, respectively.

Table 1 presents electrochemical parameters for various electrode materials tested in a $2\text{ mM K}_3[Fe(CN)_6]$ solution with 0.1 M KNO_3 at a scan rate of 50 mV s^{-1} . The study compares bare GCE, $g\text{-C}_3\text{N}_4/GCE$, $LiCoO_2/GCE$, and $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ electrodes. The $g\text{-C}_3\text{N}_4@LiCoO_2/GCE$ electrode demonstrates superior electrochemical performance across all measured parameters. It exhibits the highest anodic (I_{pa}) and cathodic (I_{pc}) peak currents, indicating enhanced electron transfer capabilities. Additionally, this electrode shows the lowest potential difference (ΔE) between anodic and cathodic peaks, suggesting improved reversibility of the electrochemical process. The performance of the electrodes can be ranked as follows:

$$g\text{-C}_3\text{N}_4@LiCoO_2/GCE > LiCoO_2/GCE > \text{bare GCE} \\ > g\text{-C}_3\text{N}_4/GCE$$

The $g\text{-C}_3\text{N}_4/GCE$ performs poorly with the lowest peak currents and highest ΔE , indicating slower electron transfer

Table 1 Electrochemical parameters of different samples were recorded at a scan rate of 50 mV s^{-1} for $2\text{ mM K}_3[Fe(CN)_6]$ containing 0.1 M KNO_3

Sample	E_{pa} (mV)	E_{pc} (mV)	I_{pa} (μA)	I_{pc} (μA)	I_{pa}/I_{pc}	ΔE (mV)
Bare GCE	271	142	15.93	-18.81	0.847	129
$g\text{-C}_3\text{N}_4/GCE$	294	067	9.19	-6.42	1.431	227
$LiCoO_2/GCE$	305	163	22.36	-20.72	0.926	142
$g\text{-C}_3\text{N}_4@LiCoO_2/GCE$	366	279	35.55	-40.38	0.828	87



kinetics and lower reversibility. The GCE and LiCoO₂/GCE electrodes demonstrate intermediate performance, with LiCoO₂/GCE generally outperforming g-C₃N₄/GCE. The outstanding performance of g-C₃N₄@LiCoO₂/GCE suggests a synergistic effect between g-C₃N₄ and LiCoO₂ when combined. This synergy improves electrochemical properties compared to the individual components or the bare electrode. The enhanced electron transfer kinetics, and stable electrochemical process make g-C₃N₄@LiCoO₂/GCE a promising electrode material for potential applications in electrochemical sensing or energy storage devices. This analysis highlights the importance of composite materials in enhancing electrochemical performance and demonstrates the potential of g-C₃N₄@LiCoO₂ as an advanced electrode material for various electrochemical applications.

Fig. 8a graph shows CV curves of g-C₃N₄@LiCoO₂/GCE in PBS (pH 7) containing 10 nM malathion at different scan rates ranging from 10 to 200 mV s⁻¹. The x-axis represents the potential (*E*) in volts vs. Ag/AgCl, ranging from -0.4 to 1.0 V. By conducting CV measurements with various scan rates ranging from 10 to 200 mV s⁻¹, the kinetic and transport characteristics of the malathion molecules on the g-C₃N₄@LiCoO₂/GCE were further characterized (Fig. 8a). The CV curves show increasing peak currents with higher scan rates, indicating a surface-controlled electrochemical process for malathion on g-C₃N₄@LiCoO₂/GCE. Regression correlations between *I*_{pa} and *I*_{pc} and the square of scan rate *v* are as follows:

$$I_{pa} = 3.544v^{1/2} - 4.466 \quad (R^2 = 0.968) \text{ and}$$

$$I_{pc} = -1.708v^{1/2} - 1.245 \quad (R^2 = 0.857).$$

The Fig. 8b suggests a surface-controlled mechanism for malathion on g-C₃N₄@LiCoO₂/GCE, rather than a diffusion-controlled process.⁵³ Table 2 presents electrochemical parameters (*E*_{pa}, *E*_{pc}, *I*_{pa}, *I*_{pc}, *I*_{pa}/*I*_{pc} ratio, and ΔE) at various scan rates, supporting the conclusion that surface adsorption primarily governs the electrochemical behavior of malathion on the modified electrode.

Table 2 Electrochemical parameters of g-C₃N₄@LiCoO₂/GCE (GL3) evaluated from the CV in PBS (pH 7) with 10 nM malathion

Scan rate (mV s ⁻¹)	<i>E</i> _{pa} (mV)	<i>E</i> _{pc} (mV)	<i>I</i> _{pa} (μA)	<i>I</i> _{pc} (μA)	<i>I</i> _{pa} / <i>I</i> _{pc}	ΔE (mV)
10	364	203	4.57	-3.74	1.222	161
25	357	254	11.41	-8.52	1.339	103
50	410	341	23.76	-16.79	1.415	69
75	437	349	29.24	-18.26	1.601	88
100	458	354	32.24	-20.48	1.574	104
125	478	365	34.11	-20.32	1.679	113
150	498	362	38.73	-21.10	1.836	136
200	519	353	43.47	-22.83	1.904	166

The DPV method, with a potential window of -0.400 to +0.800 V, a scan rate of 50 mV s⁻¹, and a sensitivity of 1.0 × 10⁻⁵ A V⁻¹, was employed to investigate the impact of malathion concentration further using C₃N₄@LiCoO₂/GCE in 0.1 M PBS under optimized conditions (Fig. 9a). The oxidation peak current at approximately 0.4 V is directly proportional to the malathion concentration. Within a range of malathion concentrations (CMA) from 5 to 120 nM, the current response on g-C₃N₄@LiCoO₂/GCE increased linearly with rising CMA. A linear regression analysis on the collected data resulted in the equation *I* = 1.632conc. + 5.949, where *I* (μA) represents the current response, showing a high correlation coefficient of *R*² = 0.99439 (Fig. 9b).

Fig. 10a displays the stability test results for DPV response signals over 16 days. The graph shows a gradual decrease in current from an initial value of 49.32 μA at day 0 to 39.91 μA at day 16. This test was conducted in a 0.1 M PBS solution (pH 7) containing 30 nM of malathion. The decreasing trend suggests a slight degradation in sensor performance over time. However, the sensor retains about 81% of its initial response after 16 days, indicating relatively good stability for the tested period. The minimal detectable concentration was determined using the formula LOD = 3σ/*m*. From the results, the standard deviation (σ) derived from 6 measurements was calculated to be

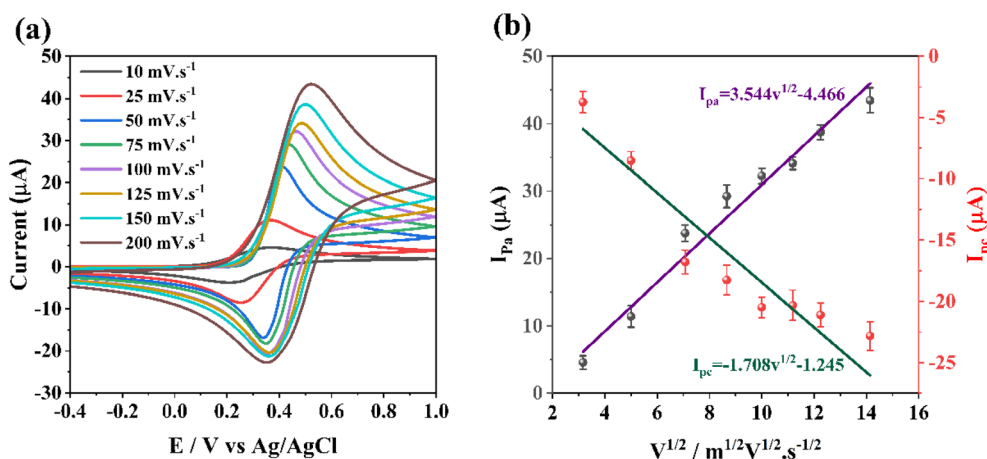


Fig. 8 (a) CV curves of g-C₃N₄@LiCoO₂/GCE in PBS (pH 7) containing 10 nM malathion at various scan rates. (b) The curves of anodic and cathodic peak currents regarding the square of scan rate.



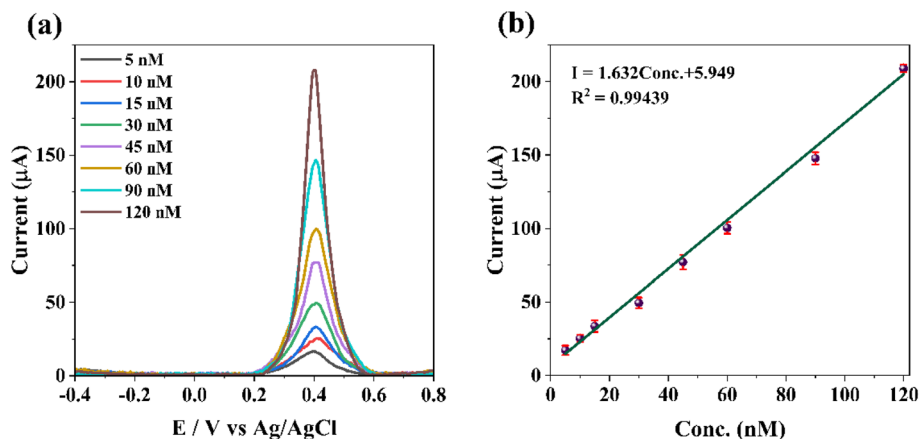


Fig. 9 (a) DPV plots for different concentrations (5–120 nM) of malathion based on the g-C₃N₄@LiCoO₂/GCE electrode at pH 7 (0.1 M PBS solution). (b) The calibration curve of DPSV current at the g-C₃N₄@LiCoO₂/GCE electrode versus malathion concentration.

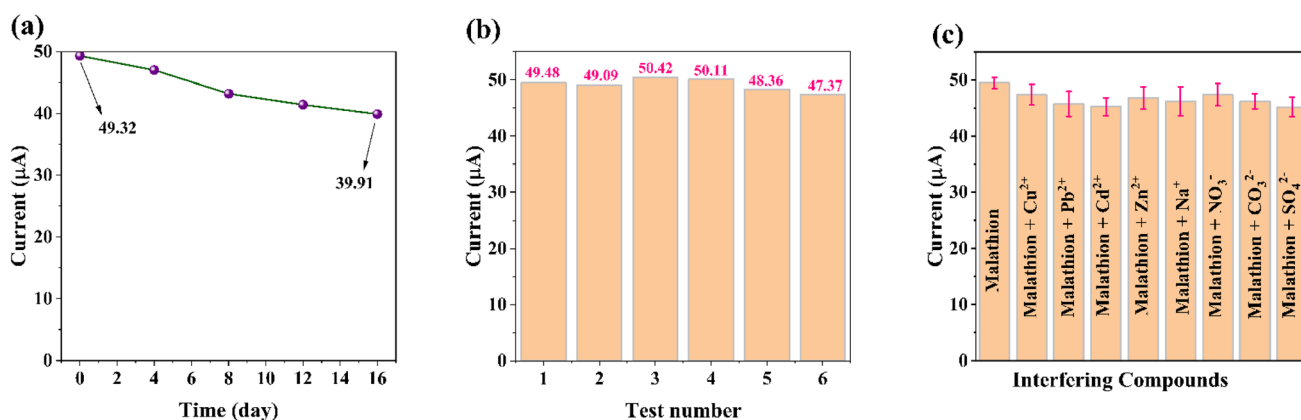


Fig. 10 (a) DPV response signals for stability test along 16 days in 0.1 M PBS (pH 7) solution in the presence of 30 nM of malathion. (b) Reproducibility of g-C₃N₄@LiCoO₂/GCE towards malathion during 6 individual tests in the presence of 30 nM of malathion (in 0.1 M PBS (pH 7) solution). (c) DPV peak current of g-C₃N₄@LiCoO₂/GCE sensor for malathion detection (30 nM) in the presence of 300 µM of different interferences. 1.632x + 5.949.

1.14 nM (Fig. 10b). In comparison, the slope (m) of the calibration curve was measured at 1.632 (Fig. 9b). Consequently, the modified electrode's minimal detection limit (LOD) within the linear range was established as 2.096 nM.^{34,55}

Fig. 10c depicts the DPV peak current density of g-C₃N₄@LiCoO₂/GCE sensor for detecting of malathion in the presence of various interfering compounds, such as Cu²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Na⁺, NO₃⁻, CO₃²⁻, and SO₄²⁻. The observed trend in Fig. 10c reveal that the g-C₃N₄@LiCoO₂/GCE sensor with an anti-interfering response is suitable for the selective detection of malathion.

Table 3 shows the measured amount of malathion based on the g-C₃N₄@LiCoO₂/GCE sensor. As listed in Table 3, the recovery range of the designed sensor for different malathion concentrations is 96.76% to 98.64%. This indicates that the electrochemical g-C₃N₄@LiCoO₂/GCE sensor can be used as a potential candidate for practical applications to detect malathion.

Table 4 illustrates the performance of the g-C₃N₄@LiCoO₂/GCE sensor was compared with that of other previously

Table 3 Recovery studies of spiked malathion in lettuce samples for g-C₃N₄@LiCoO₂/GCE electrode

Sample	Spike (nM)	I_{pa} (µA)	Found (µM)	Recovery (%)
Lettuce	00	Not found	Not found	Not found
	40	69.51	38.95	97.37
	40	69.43	38.90	97.24
	40	69.25	38.79	96.98
	80	133.22	77.98	97.48
	80	132.87	77.77	97.21
	80	134.73	78.91	98.64
	120	198.81	118.17	98.47
	120	196.38	116.69	97.24
	120	195.44	116.11	96.76

reported modified electrodes for the electrochemical measurement of malathion. Comparable to other electrodes developed by other authors, the developed electrode shown good limit of detection and linear range.



Table 4 Comparison of sensing parameters for the electrochemical detection of malathion using different electrode materials

Electrodes	Techniques	LOD	Linear range	References
CdS/g-C ₃ N ₄ /Sm-BDC/GCE	DPV	7.4×10^{-9} M	$3.0\text{--}15.0 \times 10^{-8}$ M	56
GQDs/GCE	DPV	0.62 nM	1 to 30 μ M	57
CuO/NiO/PANI	DPV	2×10^{-6} mol L ⁻¹	20–2500 mol L ⁻¹	58
Cu ²⁺ -g-C ₃ N ₄	OP	6.798 nM	70–800 nM	59
COF@MWCNT/AChE	DPV	0.5 μ M	0.001–10.0 μ M	60
g-C ₃ N ₄ @LiCoO ₂ /GCE	DPV	4.38 nM	5–120 nM	This work

4. Conclusion

Consequently, the development of a promising electrochemical probe for malathion detection based on green g-C₃N₄@LiCoO₂ nanocomposites represents a significant advancement in pesticide detection and environmental monitoring. The g-C₃N₄@LiCoO₂ nanostructures with appropriate LiCoO₂ doping can significantly enhance the electrocatalytic activity of g-C₃N₄. This improvement in electrocatalytic activity can be attributed to increased electrical conductivity, enhanced electron transfer, and an increased number of active sites on the electrode surface. Therefore, g-C₃N₄@LiCoO₂ nanostructures can serve as promising electrocatalytic materials for various electrochemical applications. This innovative sensor design offers a cost-effective and sensitive solution sensor with an acceptable recovery range for malathion probing and aligns with the growing demand for sustainable agricultural practices.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

All authors contributed equally in this paper.

Conflicts of interest

The authors declare that they have no conflict of interest.

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